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INVESTIGATION OF CHARGE-TRANSFER INTERACTIONS BETWEEN CARBON TETRABROMIDE AND AROMATIC DONORS BY GAS CHROMATOGRAPHY*

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SUMMARY

A gas chromatographic method has been employed to study the charge-transfer interactions between alkylated benzenes and molten CBr_4. Resultant activity coefficients have been analyzed in terms of the constituent intermolecular forces. Experimental results indicate a weak, but genuine charge-transfer interaction between aromatic solute and CBr_4. The charge-transfer interaction is temperature dependent, decreasing rapidly in magnitude with increasing temperature. An increasing complexation effect is noted for the addition of electron-repelling groups on the benzene nucleus.

INTRODUCTION

Investigations of charge-transfer complexation by GLC

The utilization of aromatic charge-transfer complexing in GLC was initiated in order to effect difficult aromatic isomer separations. As early as 1955, an aromatic addition complex of picric acid–fluorene was used to separate aromatic compounds[1]. In the ensuing years, many studies invoked the concept of π-electron donation of the solute to the solvent[2–6], but few could unequivocally establish that such interaction was taking place[7].

Perhaps the most extensive studies of aromatic charge-transfer complexing in gas chromatography are those of LANGER, PURNELL, and coworkers. Initially, charge-transfer complexing was inferred from unusual selectivities shown for aromatic compounds and the elution of *m*-xylene before *p*-xylene, an order not predicted on vapor pressure considerations alone[8,9]. Additional studies[10–13] with tetrahalophthalates as well as other aromatic selective liquid phases interpreted chromatographic elution parameters in terms of excess thermodynamic solution functions. Unfortunately,

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these substrates are complex in their electronic effects on solutes, so that the interpretation of excess functions is, at best, difficult. Further studies of this type employing 1,3,5-trinitrobenzene[14] and di-*n*-nonyl tetrachlorophthalate[15] as column substrates have invoked spectrophotometrically determined association constants to help explain trends in retention data.

Additional evidence indicating the value of GC in elucidating complexing phenomena has been provided by CVETANOVIC and co-workers, who studied the interaction of olefinic solutes with 1,3,5-trinitrobenzene[16]. Similarly, charge-transfer interactions have also been postulated from Rohrschneider plots[17,18], and from Kovats retention indices in a study employing molten quaternary ammonium salts as solvents[19].

Charge-transfer interaction between CBr_4 and aromatic donors

Phase studies were perhaps the first positive indication that molecular complexes could form between alkylated benzenes and CBr_4. KAPUSTINSKII AND DRAKIN[20] have examined the phase diagram of CBr_4 with benzene and found a maximum corresponding to a compound of the formula CBr_4–C_6H_6. STRIETER AND TEMPLETON[21] examined the solid adduct formed between CBr_4 and *p*-xylene by X-ray crystallography and found that their data were consistent with an orthorhombic unit cell[22] in which each planar aromatic ring is flanked on both sides by a bromine atom. The authors attributed formation of the solid adduct (m.p. 53° C) to a packing arrangement which cannot be achieved by the acceptor with other xylenes. Thus the selectivity of CBr_4 for the *p*-xylene in separation techniques[14] is spatial in nature and depends little upon the effect of the alkyl substituents in the charge-transfer interaction. This idea has been verified independently by GOATES *et al.*[15], in a study of compounds possessing similar interactions.

HOOPER[23] has studied the pure electrical quadrapole resonance frequencies of the CBr_4–*p*-xylene complex at liquid nitrogen temperatures and concluded that little, if any, charge-transfer interaction is present in the ground state. His conclusions are based on the absence of a frequency lowering for the halogen which if present would indicate a change in the electric field gradient associated with the nucleus. Nevertheless, photochemical irradiation of polyhalogenated methanes, including CBr_4, in hydrocarbon glasses reveals the production of color centers in the matrix[24]. It has been suggested that these centers are actually trapped electrons, produced from charge-transfer interactions.

Spectroscopic techniques have also been used to accumulate considerable evidence for complexing between CBr_4 and aromatic compounds. DOERR AND BUTTGEREIT[25] postulated 1:1 adducts for CBr_4 with hexamethylbenzene and mesitylene based upon the appearance of a new band in the UV spectra of these compounds. More extensive UV spectral results were obtained by TRAMER[26], who investigated the complexes formed between CBr_4 and the following donors: benzene, toluene, *p*-xylene, mesitylene, and α-chloronaphthalene. Polarization spectra of single crystal samples of the CBr_4–*p*-xylene complex were also studied. UV shifts increased as the benzene ring became more alkylated, an effect which was ascribed to charge-transfer transitions. TRAMER asserted that these were weak donor–acceptor complexes, analogous in crystal structure to the corresponding I_2 and Br_2 complexes, but much less stable.

DEMAINE[27] has pointed out the need for non-spectrophotometric studies of complex formation to verify spectrophotometric results, particularly when the associative interactions are non-color producing London and dipole–dipole interactions. HAYMANN[28] in a treatise has further questioned the reliability of spectrophotometric methods in comparison with partition methods for determining equilibrium constants of complexes. He asserts that spectrophotometric methods are affected by the formation of termolecular complexes, which do not affect the partition method provided that measurements are carried out in dilute solution.

Gas–liquid partition chromatography offers a method of studying complexing in dilute solution, *i.e.* infinitely dilute solution. Although association constants cannot always be determined by GC, analysis of solution parameters determined by GC can be extremely helpful in ascertaining complexation. Further, as noted by one author[29], GC may indeed be the preferred method of studying weak charge-transfer complexes in solution.

EXPERIMENTAL

Preparation of the columns

CBr_4 (Eastman Distillation Products Industries) having a melting point of 90–91° C was employed for this work. The support upon which the CBr_4 was distributed was Chromosorb G, a product of the Johns-Manville Corporation having a mesh range of 45/60. Coating solutions of CBr_4 were prepared by dissolving CBr_4 with gentle heating in Baker Grade (Reagent) benzene. The method of PARCHER AND URONE[30] was used to distribute the CBr_4 over the Chromosorb. At the conclusion of the fluid drying the coated support was removed carefully and weighed in a stoppered bottle. The amounts of CBr_4 deposited on the support for two different coatings were 19.02% w/w and 29.25% w/w, respectively.

The volatility of CBr_4 necessitated the use of a presaturator to replenish the solvent lost via entrainment in the carrier gas. Presaturator design and use have been adequately described in the literature[31,32]. The presaturator constructed for use in this study consisted of a copper tube, 21.1 cm in length × 1/4 in. O.D., packed with support and solvent in identical proportions to that present in the analytical column.

Instrumental parameters

The necessity of applying a presaturator column voided the use of the normal injection port provided with the commercial chromatograph, hence an injection port was constructed. It consisted of a 1/4 in. O.D., copper Swagelock tee which was wound with resistance wire connected to a rheostat. Asbestos fiber mat was used as insulation to prevent heat loss. The temperature of the injection port was monitored by an iron–constantan thermocouple embedded beneath the insulating fiber.

The injection port was placed in a steel can enclosure and insulated with glass wool. The steel can was fitted flush with an asbestos that covered the oven of the gas chromatograph. A small hole was drilled into the board, concentric with the injection septum mounted in the Swagelock tee. This arrangement when placed in the column oven produced little effect on the SCR controller of the commercial instrument.

The flow pattern is illustrated in Fig. 1. Helium was employed as a carrier gas. In order to minimize gas phase non-ideality in the analytical column, the ratio of p_i/p_0 was kept at approximately 1.15. The Moore flow controller supplied with the gas chromatograph, soap bubble flow meter for measuring outlet flow rates, and U-

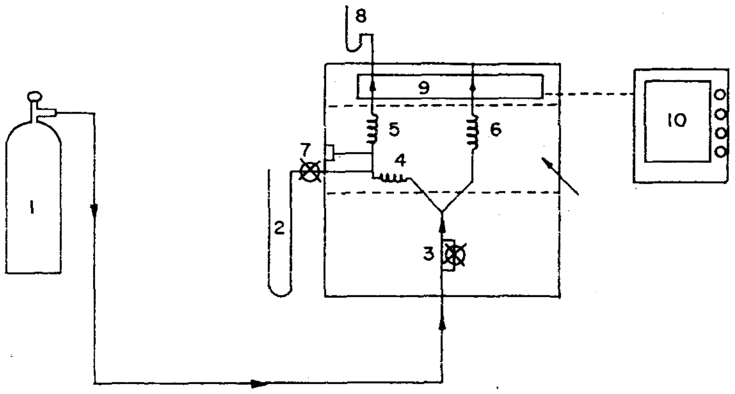

Fig. 1. Experimental flow schematic. 1 = Carrier gas supply; 2 = manometer; 3 = flow controller; 4 = presaturator; 5 = analytical column; 6 = dummy column; 7 = injection port; 8 = flow meter; 9 = thermal conductivity cell; 10 = recorder. Dotted lines indicate thermostatted chamber.

tube manometer for reading inlet pressure were all thermostatted to ± 0.5° C.

The commercial gas chromatograph employed with the above described modifications was a Varian Aerograph Model 202. The detection unit was a dual thermal conductivity cell employing WX filaments. Differential displays of the elution profiles were recorded by a Sargent Model SRL recorder. Chart paper was kept and measured in a room controlled to ±0.5° C in order to prevent expansion or contraction of cellulose fibers.

Temperature measurement

Temperature measurement was accomplished with the apparatus schematically illustrated in Fig. 2. The potentiometer employed was a Leeds & Northrup Model K with a range of 5 V to 1 mV. A D'Arsonval-type galvanometer, Leeds & Northrup Model No. 2430, was employed as a null detector. Its CDRX was 2100 Ω, internal

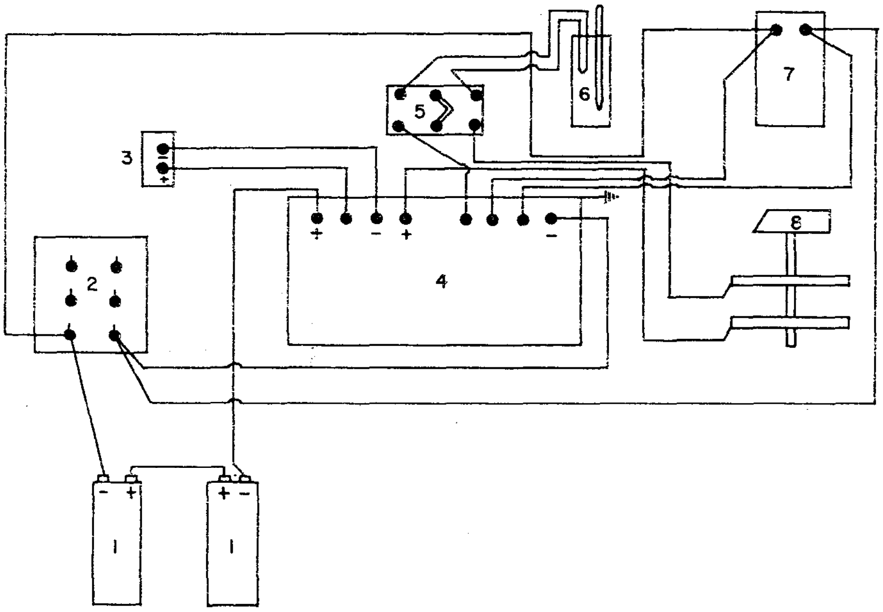

Fig. 2. Electrical measurement schematic. 1 = Dry cells; 2 = resistance box; 3 = standard cell; 4 = potentiometer; 5 = switch; 6 = ice point reference; 7 = galvanometer; 8 = rotary switch.

TABLE I

INSTRUMENTAL PARAMETERS REQUIRED FOR THE CALCULATION OF RETENTION DATA

Property	*93.7 °C*	*104.5 °C*	*105.3 °C*	*113.9 °C*	*123.6 °C*
F (ml/min)	26.2	27.0	31.5	32.0	24.7
T (°K)	366.8	377.7	378.5	387.1	396.8
T_a (°K)	296.2	292.6	296.8	296.8	292.6
p_w (mm Hg)	21.0	19.4	21.8	21.8	19.4
$p_a = p_o$ (mm Hg)	734.0	734.0	737.8	737.8	734.0
F_c (ml/min)	31.5	34.0	39.0	40.5	32.6
p_i (mm Hg)	841.0	841.0	832.0	887.2	841.0
j (unitless)	0.930	0.930	0.939	0.795	0.930
w (g)	6.5209	6.5209	6.1095	6.1095	6.5209

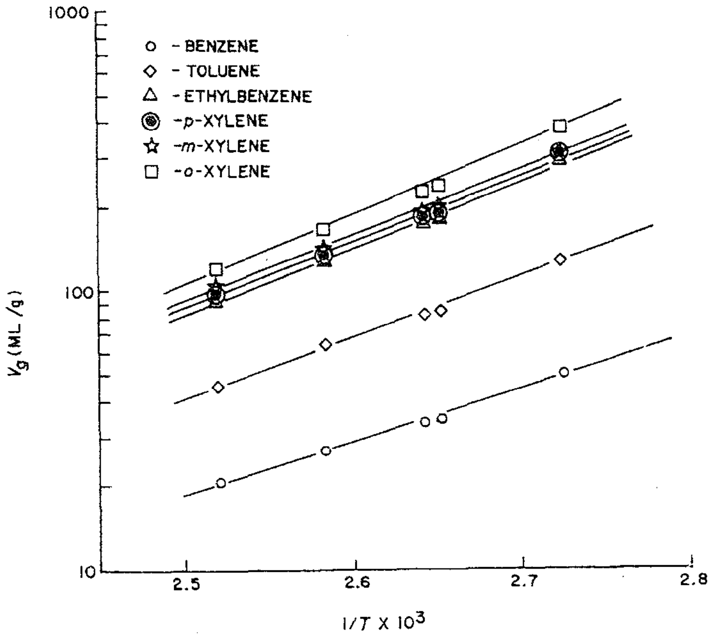

Fig. 3. Specific retention volume *vs.* reciprocal temperature.

TABLE II

SPECIFIC RETENTION VOLUMES *VS.* TEMPERATURE FOR AROMATIC DONORS IN CBr_4

All figures are in units of ml/g.

Compound	*93.7 °C*	*104.5 °C*	*105.3 °C*	*113.9 °C*	*123.6 °C*
Benzene	48.5	33.8	33.2	26.2	20.6
Toluene	123.5	80.6	79.1	62.4	44.9
Ethylbenzene	279.4	172.1	168.3	123.4	91.1
m-Xylene	305.5	188.9	184.5	136.7	101.5
p-Xylene	299.0	183.4	178.9	131.9	97.4
o-Xylene	365.1	224.3	219.0	158.6	118.9

resistance 25 Ω, giving it a period of 2.7 sec. The d.c. source for this circuit consisted of two 1½-V dry cells. A reference potential was provided by an Epley Student Cell having a rating of 1.0183 V. Variable resistance was provided by a Leeds & Northrup decade box ranging from 0.1–10^3 ohms. A rotary switch with six insulated iron–constantan thermocouples was used to monitor temperature.

Experimental procedure

Solutes were obtained from two sources: the benzene, toluene, and ethylbenzene were Phillips 99 mole % grade while the xylene isomers were obtained courtesy of Sinclair Petrochemicals, Inc. All solutes were used without further purification. The dependence of the solute retention on sample size was checked by varying the injection sample size. Variance of the sample size for a tenfold range (1.0–0.1 μl) produced no change in retention volume or peak symmetry.

The temperature of the injection block was kept at 230° C while the compartment housing the T.C. bridge registered 204° C on the pyrometer gauge. Cell currents were consistently 133 mA. Outlet flow rates ranged from 25–40 ml/min. Temperature fluctuations of the oven bath were minimized to ±0.1° C at 93.7° C and to ±0.15° C at 113.9° C. The latter figures were obtained by a time *versus* temperature fluctuation study of various thermocouple probes.

Analysis of each solute was done in triplicate employing 0.1-μl sample sizes. Although some of the retention times were extremely long at this relatively slow flow rate, the accuracy gained in being able to reproduce retention times gave further credence that equilibrium conditions were prevailing in the column. Retention times were converted to specific retention volumes, V_g, using the following equation:

$$V_g = jF_c 273(t_R - t_A)/w_L T \qquad (1)$$

where

j = gas compressibility factor
F_c = corrected flow rate
t_R = retention time of solute
t_A = retention time of unsorbed solute
w_L = solvent weight
T = column temperature

The numerical quantities required for these calculations are listed in Table I. Specific retention volumes have been tabulated in Table II.

It is perhaps pertinent to note the variance of V_g with column temperature. This is depicted in Fig. 3. The ability to reproduce V_g independent of solvent weight is clearly shown in the close agreement of V_g at 104.5° C and 105.3° C. Thus, activity coefficients at infinite dilution, γ^∞, can be calculated with confidence and used to interpret solution processes.

RESULTS AND DISCUSSION

Specific retention volumes were used to calculate activity coefficients at infinite dilution by using eqn. 2

$$V_g = 273R/p^0M_L\gamma^\infty \tag{2}$$

where

p^0 = saturated vapor pressure of solute at column temperature
M_L = molecular weight of solvent
R = 6.3×10^4 ml-mm/mole-°K

Vapor pressure values were computed using the well-known Antoine equations of the form

$$\log_{10}p^0 \text{ (in mm Hg)} = A - (B/t + C) \tag{3}$$

where t is the temperature of the column in °C and A, B, C are the Antoine constants for the solute[33]. The derived activity coefficients at infinite dilution are listed in Table III.

TABLE III

ACTIVITY COEFFICIENT AT INFINITE DILUTION *vs.* TEMPERATURE FOR AROMATIC DONORS IN CBr_4
All figures are unitless.

Compound	*93.7 °C*	*104.5 °C*	*105.3 °C*	*113.9 °C*	*123.6 °C*
Benzene	0.939	0.994	0.994	1.007	1.015
Toluene	0.915	0.998	0.995	0.984	1.053
Ethylbenzene	0.894	0.998	0.996	1.035	1.052
m-Xylene	0.902	0.998	0.997	1.020	1.027
p-Xylene	0.894	1.000	1.000	1.031	1.045
o-Xylene	0.892	0.986	0.985	1.027	1.036

Activity coefficients can yield much information on the intermolecular forces that are present in solution. Further, the activity coefficient also reflects the superimposition of size effects in the liquid state. From basic thermodynamics, the definition of the excess partial molar free energy, $\Delta\bar{G}_e{}^0$, is

$$\Delta\bar{G}_e{}^0 = RT \ln \gamma^\infty = \Delta\bar{H}_e{}^0 - T\Delta\bar{S}_e{}^0 \tag{4}$$

from which it can be shown that

$$\delta\Delta\bar{G}_e{}^0/\delta T = -\Delta\bar{S}_e{}^0 \tag{5}$$

and

$$\delta(\Delta\bar{G}_e{}^0/T)/\delta(1/T) = \Delta\bar{H}_e{}^0 \tag{6}$$

where $\Delta\bar{H}_e{}^0$ and $\Delta\bar{S}_e{}^0$ are the excess partial molar enthalpy and entropy of solution, respectively. Eqn. 4 may be rewritten in the form

$$\ln \gamma^\infty = \Delta\bar{H}_e{}^0/RT - \Delta\bar{S}_e{}^0/R \tag{7}$$

which suggests that the activity coefficient may be regarded as a composite function, or as expressed by ASHWORTH AND EVERETT[34]

$$\ln \gamma^\infty = \ln \gamma^s + \ln \gamma^e \tag{8}$$

where $\ln \gamma^e$ and $\ln \gamma^s$ are the thermal and the athermal contribution to the activity coefficient.

The sign and magnitude of the partial molar excess enthalpy of solution can be extremely difficult to interpret, especially if either the solute or the solvent are structurally complex. PURNELL AND LANGER[12,35] have recognized that $\ln \gamma^e$ is a composite of heats, $\Delta \bar{H}_{e\alpha}{}^0$, $\Delta \bar{H}_{e\beta}{}^0$, etc., some of which may be favorable to solution (negative) and others positive, forcing the molecules of solute out of the liquid phase. Thus, the fact that $\Delta \bar{H}_e{}^0$ is not negative in sign does not imply that complexing forces are not operative in solution. Further, large positive enthalpic contributions may mask out energetically weak complexing interactions which give rise to negative deviations from Raoult's Law.

Inspection of the activity coefficient values in Table III reveals a trend at 93.7° C supporting increasing charge-transfer interaction with alkylation of the benzene ring. This trend completely disappears at higher temperatures. Therefore, it seems strange that the apparent drop-off in complexing ability is abrupt and not temperature dependent.

Various association parameters can be obtained by comparing the elution data (*e.g.* V_g) of solutes capable of undergoing charge-transfer complexing on an inert solvent *versus* their V_g values on a charge-transfer complexing solvent. By use of eqn. 9

$$V_g = 273R/\gamma' p^0 M_L \tag{9}$$

MARTIRE AND RIEDL[36] have been able to calculate the equilibrium constant of hydrogen-bond formation as well as the corresponding enthalpies of formation. Here γ' is the apparent (measured) activity coefficient which is defined as

$$\gamma' = \gamma_u(1 - c) \tag{10}$$

where γ_u is the activity coefficient at infinite dilution, and c is the fraction of solute molecules complexed. To measure γ_u requires specific retention volumes determined on an analogous non-complexing stationary phase. For CBr_4, the non-complexing analog would be CH_4, which at the temperatures employed in this study would be extremely difficult to use as a liquid phase.

An alternative procedure would be to assume that γ_u is approximately the same for a number of structurally similar solutes. Thus, following the procedure adopted by LANGER *et al.*[9], one could assign a value of unity to $(1 - c)$ and measure relative complexing tendency to a particular solute. If this is done for the data in Table III at 93.7° C and the assignment of $(1 - c) = 1$ is for benzene, then c increases as alkylation of the benzene ring increases. However, following this procedure for solutes at higher temperatures gives anomalous results.

It may well be that molecular size differences account for the results at higher temperatures. Recalling eqns. 7 and 8, it can be shown that

$$\ln \gamma^s = -\Delta \bar{S}_e{}^0/R \tag{11}$$

Using the Flory–Huggins approach, at infinite dilution

$$\gamma^s = (1/m)\, e^{1-(1/m)} \tag{12}$$

where $m = v_2/v_1$ and v_2 and v_1 are the molar volumes of solvent and solute, respectively, the contribution to γ^{∞} from γ^{s} is negligible in the case for our solutes ($\ln \gamma^{s} = 1$). This is not surprising since the molar volumes of the solute and solvent in this experiment are nearly equal. Hence the activity coefficient at infinite dilution is directly related to the thermal portion of the activity coefficient or

$$\gamma^{\infty} = \gamma^{e} \qquad (13)$$

The general form of $\ln \gamma^{e}$ is given by eqn. 14

$$\ln \gamma^{e} = k\Delta E \qquad (14)$$

where ΔE is the summation of molar interchange energies. Thus $\Delta \bar{H}_{e}{}^{0}$ can be regarded as a sum of pairwise potential energies of interaction between solute and solvent molecules, or in general

$$\ln \gamma^{e} = k(E_{11} + E_{22} - 2E_{12}) \qquad (15)$$

As BROWN[37] has pointed out, E_{12} is predominantly a measure of electron donor–acceptor interactions between solute and solvent. Thus, if one could obtain a general equation for the calculation of γ^{e}, the strength of E_{12} could be ascertained.

In 1961, MARTIRE[38] derived the following equation from the Van Arkel modification of Hildebrand's regular solution theory

$$\ln \gamma^{e} = (v_1\varphi_2{}^2/RT)\,[(\delta_1 - \delta_2)^2 + (\omega_1 - \omega_2)^2 - K] \qquad (16)$$

where

φ_2 = volume fraction of solvent in solution
δ_2 = solubility parameter of the solvent
δ_1 = solubility parameter of the solute
ω_2 = orientation parameter of the solvent
ω_1 = orientation parameter of the solute
K = residue force parameter

Although originally proposed for the prediction of activity coefficients, MARTIRE's equation allows the estimation of molecular forces present in solution. Further, the above equation shows remarkable ability to predict accurate activity coefficients at infinite dilution and has been employed with success by several workers[39,40].

A regular solution is one involving no entropy change when a small amount of solute is transferred to it from an ideal solution of the same composition. Initially, regular solution theory was applied only to molecules displaying dispersion force interaction in solution. To account for other forces, such as orientation fields, the Hildebrand–Scatchard expression for the activity coefficient, eqn. 17, must be modified.

$$\ln \gamma^{\infty} = (v_1/RT)\varphi_2{}^2\,(\delta_1 - \delta_2)^2 \qquad (17)$$

By adding terms characteristic of the positive and negative heats, activity coefficients less than unity become possible to predict. Despite the many assumptions in the regular solution theory, it has worked remarkably well for correlating solution behavior. In gas chromatography alone, the regular solution theory has been applied to predict activity coefficients[41–43], correlate retention data[44,45], and in the selection of liquid phases[35,46].

Inspection of eqn. 16 reveals some very interesting details. If γ^{∞} is known and the contribution of dispersion forces, $(\delta_1 - \delta_2)^2$, and orientation forces, $(\omega_1 - \omega_2)^2$, can be estimated, then it should be possible to calculate K, the residue force parameter. If CBr_4 is undergoing charge-transfer interaction with the benzene ring, then K should reflect these interactions, since charge-transfer interactions are known to give negative deviations from Raoult's Law[47]. Further, in this specific complexing case, K should reflect the electron donor–acceptor interaction solely since it has already been shown that size effects do not contribute to $\ln \gamma^{\infty} < 1$.

The quantity $(\delta_1 - \delta_2)$ requires knowledge of the variance of δ with temperature. The solubility parameter, δ, is a measure of the cohesive energy density of the molecular species under consideration. Since δ is defined as

$$\delta = (\Delta E^{vap}/v)^{\frac{1}{2}} \tag{18}$$

the variation of the solubility parameter with temperature is related to the density dependence of v, the molar volume. Employing eqn. 19 (ref. 48)

$$\mathrm{d} \ln \delta / \mathrm{d} \ln v = -1.25 \tag{19}$$

and integrating

$$\ln \delta_{T_2} - \ln \delta_{T_1} = -1.25 \ln (v_{T_2}/v_{T_1}) \tag{20}$$

yields the desired relationship between δ and T. Solubility parameters, δ_T and v_T were selected from HILDEBRAND AND SCOTT[49]. The computation of δ_{T_2} for CBr_4 was made employing the Clausius–Clapeyron equation

$$\mathrm{d} \ln p^0/\mathrm{d}T = \Delta H^{vap}_{app}/RT^2 \tag{21}$$

using P-V-T data[50]. Calculation of δ_2 was then facilitated by employing eqn. 22

$$\delta \cong [(\Delta H^{vap}_{app} - RT)\, Z/v]^{\frac{1}{2}} \tag{22}$$

Values of δ are listed in Table IV, while the square of the difference in the solubility parameters, $(\delta_1 - \delta_2)^2$, are tabulated in Table V.

The orientation parameter, ω, is estimated from the expression for the average energy of a point dipole in a liquid, eqn. 23, to be

$$e = 2\mu^4/3r^6kT \tag{23}$$

TABLE IV

δ *vs.* TEMPERATURE

All figures are in units of cal. $^{0.5}$/cc.$^{1.5}$.

Compound	*93.7 °C*	*104.5 °C*	*105.3 °C*	*113.9 °C*	*123.6 °C*
Benzene	8.22	7.98	7.97	7.90	7.78
Toluene	8.09	7.90	7.92	7.82	7.63
Ethylbenzene	8.01	7.87	7.87	7.75	7.65
m-Xylene	7.97	7.91	7.91	7.83	7.78
p-Xylene	7.99	7.86	7.85	7.74	7.65
o-Xylene	8.23	7.98	7.98	7.90	7.77

TABLE V

$(\delta_1 - \delta_2)^2$ *vs.* TEMPERATURE

All figures are in units of cal./cc.

Compound	*93.7 °C*	*104.5 °C*	*105.3 °C*	*113.9 °C*	*123.6 °C*
Benzene	0.030	0.078	0.078	0.123	0.212
Toluene	0.032	0.130	0.109	0.185	0.372
Ethylbenzene	0.068	0.152	0.144	0.250	0.348
m-Xylene	0.090	0.123	0.116	0.176	0.212
p-Xylene	0.078	0.160	0.160	0.260	0.348
o-Xylene	0.002	0.078	0.073	0.160	0.221

where

r = distance between dipole centers
μ = the dipole moment of the molecule

The activity coefficient at infinite dilution must be unitless, so provided that ω^2 must have units of energy/volume, the average orientation energy must be divided by the volume for unit consistency. Hence

$$\omega = \mu^2(2/3vr^6kT)^{\frac{1}{2}} \tag{24}$$

making

$$(\omega_1 - \omega_2)^2 = \frac{2N^4\,[\mu_1{}^2/(v_1)^{\frac{1}{2}} - \mu_2{}^2/(v_2)^{\frac{1}{2}}]}{3RT\,r^6\,(4.18 \times 10^7)^2} \tag{25}$$

where N is Avogadro's number and k is the Boltzmann constant.

Considering the spherical symmetry of CBr_4, the Clusius–Weigand model employed by MARTIRE is equally applicable here. This model assumes a spherical molecule in the force field of six other molecules. The value predicted by the model for a body-centered lattice is

$$v_2 = (3)^{9/4}r^3/(2)^{7/2} \tag{26}$$

or

$$[\{v_2 \times (2)^{7/2}/(3)^{9/4}\}^{1/3}]^6 = r^6 \tag{27}$$

which yields

$$r^6 = (v_2{}^2/1.047) \tag{28}$$

Thus, the final expression for $(\omega_1 - \omega_2)^2$ is

$$(\omega_1 - \omega_2)^2 = \frac{3.40 \times 10^7}{v_2{}^2\,RT}\left(\frac{\mu_1{}^2}{\sqrt{v_1}} - \frac{\mu_2{}^2}{\sqrt{v_2}}\right)^2 \tag{29}$$

For the solute–solvent system in this study, contributions to $\ln \gamma^\infty$ from $(\omega_1 - \omega_2)^2$ are small, and in many cases zero. The μ for CBr_4, benzene, and *p*-xylene is zero in deference to their spherical symmetry, while the μ for toluene (0.4 D), ethylbenzene (0.36 D), *m*-xylene (0.32 D), and *o*-xylene (0.52 D) are very small[51]. Nonetheless, $(\omega_1 - \omega_2)^2$ has been calculated and is presented in Table VI.

K values are listed in Table VII. Numerically, the value of K increases as the

TABLE VI

$(\omega_1 - \omega_2)^2$ *vs.* TEMPERATURE
All figures are in units of cal./cc.

Compound	*93.7 °C*	*104.5 °C*	*105.3 °C*	*113.9 °C*	*123.6 °C*
Benzene	0	0	0	0	0
Toluene	0.055	0.053	0.053	0.051	0.049
Ethylbenzene	0.033	0.029	0.029	0.039	0.037
m-Xylene	0.032	0.031	0.031	0.031	0.035
p-Xylene	0	0	0	0	0
o-Xylene	0.087	0.084	0.084	0.082	0.079

benzene ring becomes alkylated. Thus, increasing the electron density of the ring contributes significantly to the donor–acceptor interaction. Table VII also reflects the dependence of charge-transfer interaction on temperature. For practically all solutes employed in this study, there is a seven- to eightfold decrease in charge-transfer interaction in going from 93.7° C to 123.6° C. The similarity of K values for ethylbenzene and the xylenes follows random trends observed in other charge-transfer studies[52]. Apparently, there is no special selectivity for *p*-xylene in molten CBr_4. This lends further substantiation to arguments that the formation of a CBr_4–*p*-xylene addition compound is a result of packing geometry and not particularly strong charge-transfer interaction.

TABLE VII

K VALUES *vs.* TEMPERATURE
All figures are in units of cal./cc.

Compound	*93.7 °C*	*104.5 °C*	*105.3 °C*	*113.9 °C*	*123.6 °C*
Benzene	0.489	0.120	0.120	0.067	0.068
Toluene	0.589	0.144	0.144	0.080	0.083
Ethylbenzene	0.683	0.165	0.165	0.092	0.095
m-Xylene	0.686	0.164	0.164	0.091	0.092
p-Xylene	0.688	0.166	0.163	0.093	0.095
o-Xylene	0.651	0.159	0.159	0.089	0.092

How strong are these charge-transfer forces in liquid CBr_4? A measure of this can be found by comparing K for the CBr_4–benzene complex with the K for a well-known charge-transfer complex, for example I_2–benzene. If one takes the difference in solubility parameters for I_2 and benzene at 25°C, $(\delta_1 - \delta_2)^2 = 24.5$ cal./cc, and assuming $(\omega_1 - \omega_2)^2 = 0$, then $K > 24.5$ cal./cc for this system to exhibit a negative deviation from Raoult's Law. Thus, the CBr_4–benzene charge-transfer interaction is indeed a weak one at elevated temperatures.

CONCLUSION

There is apparently a weak, but genuine charge-transfer interaction between aromatic solute and CBr_4 under the conditions employed in this set of experiments.

This is in agreement with the earlier mentioned phase studies and spectral data. The charge-transfer interaction is temperature dependent, decreasing rapidly in magnitude with increasing temperature. K values determined by the latter method show an increasing complexation trend with the addition of electron-repelling groups on the benzene nucleus. The apparent selectivity of CBr_4 for *p*-xylene so evident in the solid state is absent at these temperatures. Thus, factors other than charge-transfer interaction are responsible for the *p*-xylene–CBr_4 addition complex.

The method presented here for determining charge-transfer complexing is, in theory, applicable to other types of intermolecular forces that cause negative deviations from Raoult's Law, *i.e.* hydrogen bonding. Several requirements will have to be observed, however:

(1) Size effects must be accounted for. This is made possible by subtracting out the γ^s contribution to γ^∞ via eqn. 8.

(2) Accurate δ and ω parameters must be obtained.

(3) K must reflect a dominant force which gives rise to negative departures from solution ideality.

Point (1) is readily obtainable through experiment or statistical–mechanical formulations. Point (2) should present little problems for well characterized molecules. Point (3) of course can only be verified by continuous application to a wide variety of solute–solvent systems. Present work indicates its applicability may be more universal than previously thought. In theory, the above results are internally consistent with the results obtained for electron donor–acceptor interaction using the method advocated by ROHRSCHNEIDER[53] and the extraction postulates of PRAUSNITZ and coworkers[54].

In summary, the above method for ascertaining complexing may be particularly useful when Class A, Class D, and comparative Class B methods, as defined by PURNELL[55], are not applicable. This especially would be the case for volatile solvents where there is a lack of an "inert solvent" for experimentally determining the dispersion contribution to the activity coefficient.

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